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Production of higher alcohols from CO and H₂

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Combined mechanistic and catalytic reactor studies were applied to gain mechanistic insights into the catalytic cycle of producing C₂-oxygenates (C₂-O) from CO and H₂ over supported single metallic Rh catalysts.

Background

Supported metallic Rh has been shown to form C₂-O with a wide range of selectivities and CO conversion levels [1,2]. The present study seeks to understand the origin of this wide spread and become able to make catalysts with high C₂-O selectivity at simultaneous high syngas conversion at an acceptable level of metal loading.

Catalytic performance during the CO-H₂ reaction for 1% Rh dispersed on SiO₂ or ZrO₂ – impact of CO/H₂ pressure

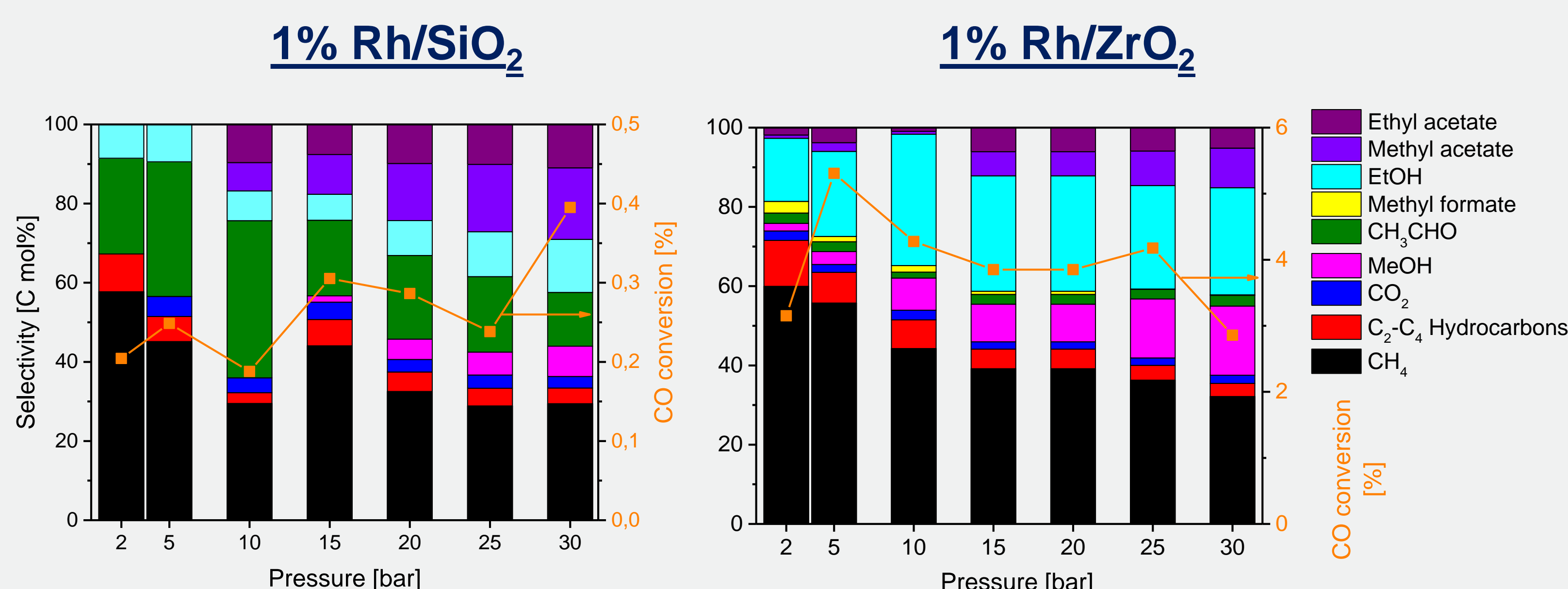


Figure 1: Product distribution and CO conversion as a function of the CO/H₂ gas feed pressure for the CO-H₂ reaction over 1% Rh/SiO₂ (left) and 1% Rh/ZrO₂ (right). Catalysts were prepared via wet impregnation of Rh(NO₃)₃ solution. $m_{\text{cat}} = 2.00$ g, flow = 37 SmL/min, $T_{\text{Rh/SiO}_2} = 250$ °C, $T_{\text{Rh/ZrO}_2} = 225$ °C.

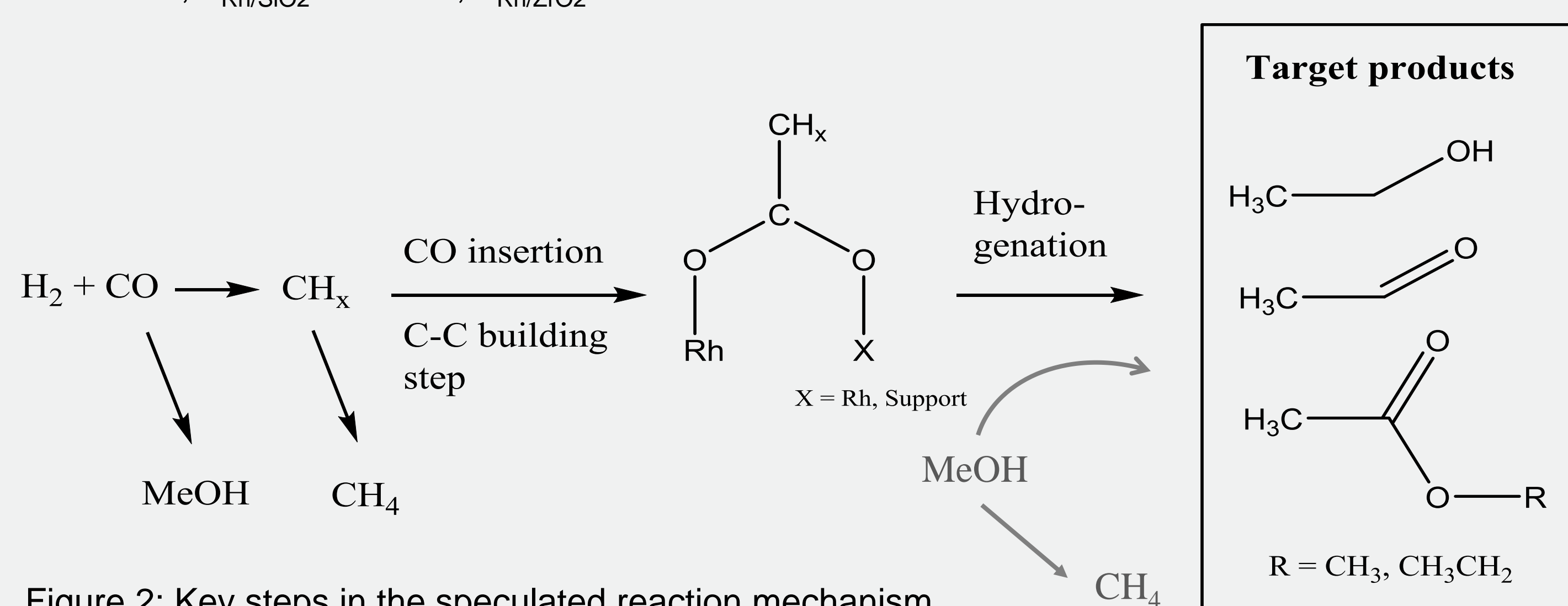


Figure 2: Key steps in the speculated reaction mechanism.

- Elevated CO/H₂ gas feed pressure is required to obtain C₂-oxygenates as majority product over Rh catalysts.
- The choice over the support has a strong impact on the CO conversion level (ca. tenfold increase for ZrO₂ compared to SiO₂-supported Rh).
- Further elevated CO/H₂ pressure conditions shifts the distribution within C₂-O products (AcH/EtOH/acetate esters).

Role of in situ formed MeOH as reactant

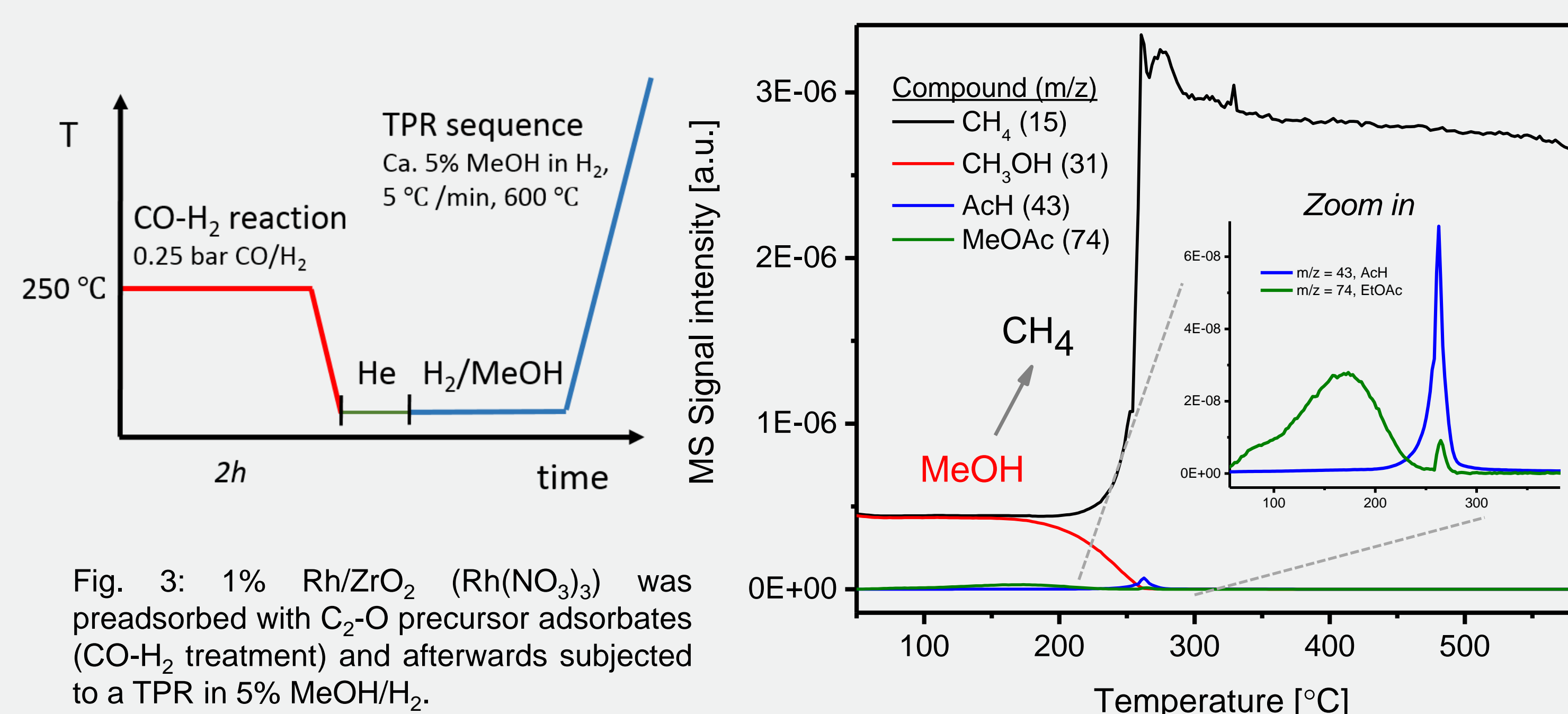


Fig. 3: 1% Rh/ZrO₂ (Rh(NO₃)₃) was preadsorbed with C₂-O precursor adsorbates (CO-H₂ treatment) and afterwards subjected to a TPR in 5% MeOH/H₂.

Significant levels of ester products were found at high CO/H₂ pressure conditions. It was shown, that surface C₂-O precursor adsorbates can react in a H₂/MeOH atmosphere to methyl acetate.

Topological changes to the Rh catalyst

RhCl₃-derived catalysts are reported to be better C₂-O producing catalysts. Remaining Cl is assumed to mobilize the Rh through involvement in formation of Rh-carbonyl complexes.

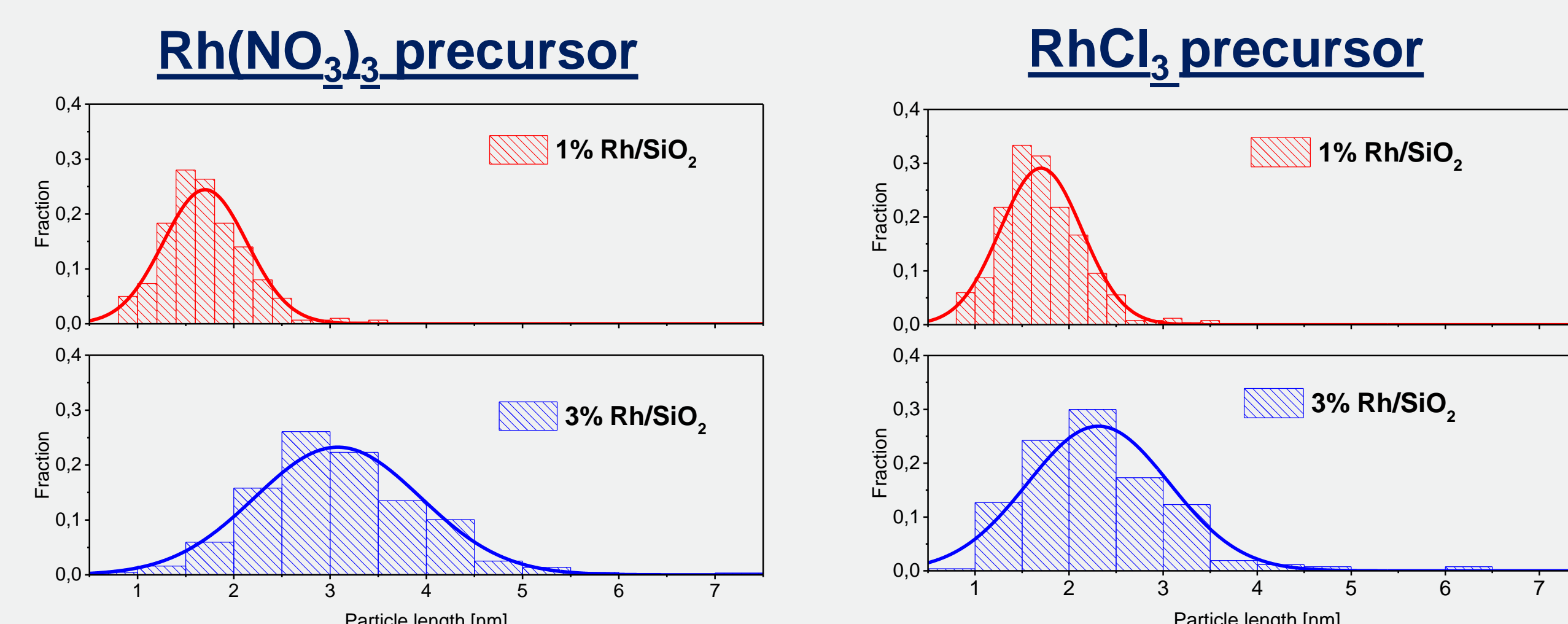


Figure 4: TEM derived particle size distribution analysis imaging for 1 and 3 wt% loaded Rh/SiO₂ catalysts from Rh(NO₃)₃ (left) and RhCl₃ (right) as precursor material.

- 50 bar CO-H₂ reaction treatment of 3% Rh/SiO₂ (from RhCl₃) resulted in a complete depletion of the Rh. Most likely due to volatility of formed carbonyls.

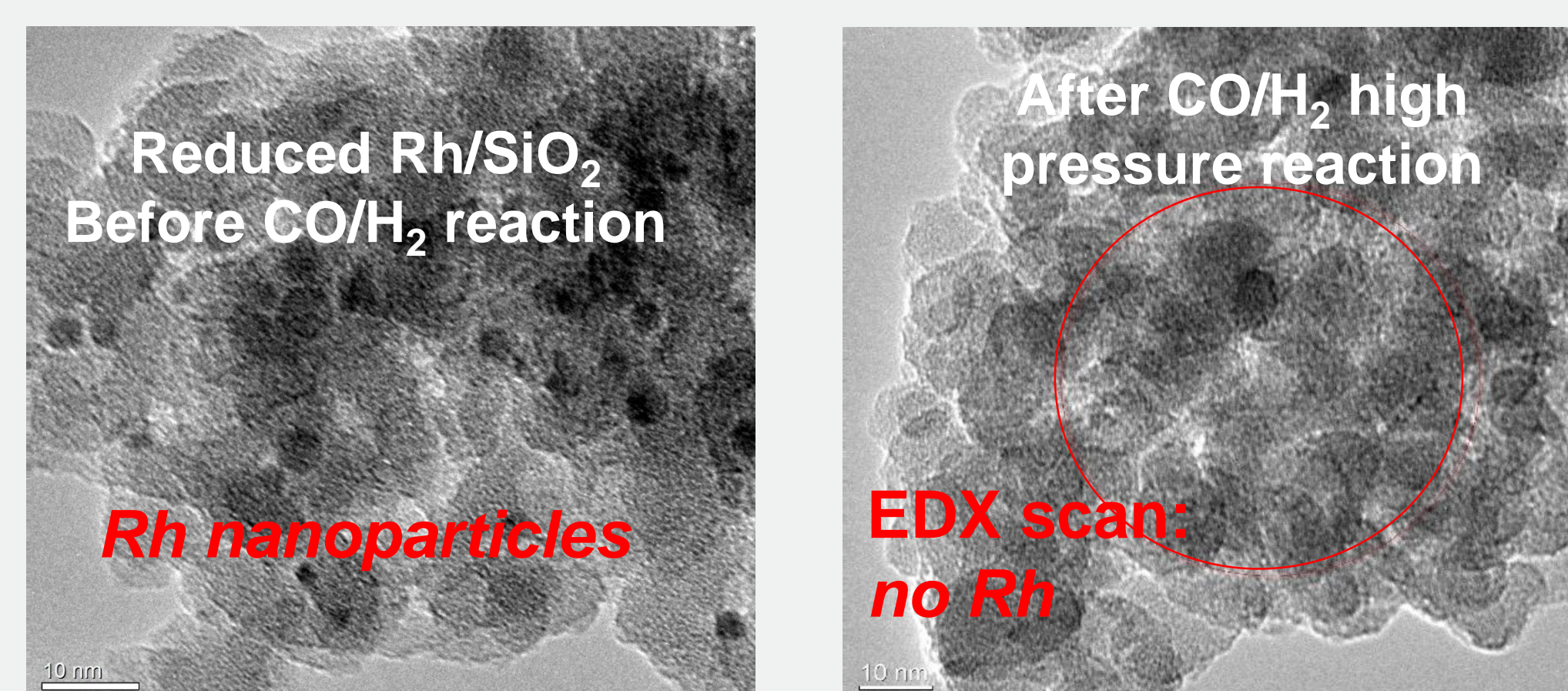


Figure 5: TEM images of 3% Rh/SiO₂ (from RhCl₃) before (left) and after (right) CO-H₂ reaction at 50 bar, 275 °C.

Outlook

- In situ EXAF: Rh/support exposed to different CO pressures.
- Environmental TEM – identifying possible topological changes of the Rh during the exposure to CO atmospheres.

References

- Ichikawa, J. Chem. Soc. Chem. Comm. **1978**, 13, 566.
- Bhasin et al., J. Catal. **1978**, 54, 120.